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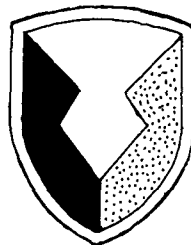
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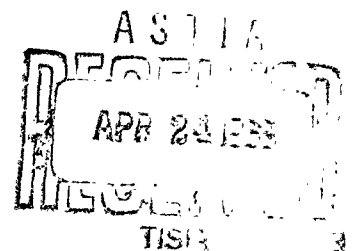
APPLICATION OF THE INTERNAL STANDARDIZATION METHOD FOR THE
GAS CHROMATOGRAPHIC DETERMINATION OF DRYING OIL FATTY ACIDS

BY

GEORGE G. ESPOSITO

AMCMS CODE NO. 5026.11.84205
DA PROJECT I-H-O-24401-A-110-05

20 MARCH 1963



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ABSTRACT

This investigation was conducted to determine a suitable method for obtaining quantitative data from the chromatographic separation of methyl esters prepared from oils used in organic coatings. The internal standard method is compared to the total area technique and found to be necessary for accurate analysis.

The sample is saponified and the fatty acids isolated. A known weight of margaric acid, the internal standard, is added to a known amount of sample followed by methyl ester formation and separation of the esters on a polyester column by gas chromatography. The unreacted fatty acids are calculated individually and materials, such as dimers, trimers and adducts are determined by difference.

1. INTRODUCTION

Gas chromatography has been used as an analytical tool to determine the fatty acid composition of oils and fats by separation of methyl esters on various polyester columns. Most of the data found in the literature uses the normalization of peak areas (total area) as the method of quantitative analysis. In this method the total area under a chromatogram is assumed to represent all the material in the sample. Since some of the fatty acids present in drying oils are of the polyunsaturated type, it was logical to assume that some reaction would occur during the preparation of coating resins which would render them unsuitable for chromatographic analysis by the total area method. Treatment of oils; such as heat bodying and reaction with unsaturated monomers, is commonly practiced to produce high molecular weight compounds of fatty acids which are conducive to forming rapid drying coating materials. Drying oils are used in the preparation of alkyd resins and during the process are subjected to considerable heat, causing reaction of some polyunsaturated acids. In order to account for the reacted unsaturated fatty acids, an investigation was initiated to determine the applicability of the internal standard method to this type of material.

A modified total area method (7) was reported for the determination of polymerized fatty acids by a technique requiring precise sampling of known mixtures of pure methyl esters and comparing the total area obtained to that of an equal volume of sample, the difference being attributed to polymerized fatty acids. This method requires daily calibration and is based on exact sampling, which introduces error into the method and provides an approximation of polymerized fatty acids.

The use of an internal standard has been reported for the determination of fatty acids in meat fat (3) and the fatty acid content of milk (2). Iden and Kahler (5) used methyl margarate, as an internal standard, for the determination of fatty acids in tall oil and found some to contain as low as 85% fatty acids. The use of an internal standard for the determination of fatty acids in drying oils could not be found in the literature and is the subject of this investigation. The amounts of reacted and unreacted fatty acids found in alkyd resins, heat bodied oils and cyclopentadiene treated oils by the internal standard method are shown in this report.

The method employed in this study is essentially the one used by Iden and Kahler (5) for the determination of tall oil fatty acids with changes made for the isolation of fatty acids and preparation of methyl esters. The resin was saponified using the ASTM unsaponifiable method D555-54 and the unsaponifiable was removed before isolating the fatty acids. A weighed amount of margaric acid was added to a known weight of fatty acids and methyl esters were prepared using boron trifluoride etherate in methanol and the methyl esters were separated on a polyester column. An inert gas was used at all stages to protect the fatty acids from oxidation by the atmosphere.

II. DETAILS OF TEST

Chromatographic Unit

The equipment used to obtain the chromatograms was a Model 500 Linear Programmed Temperature Gas Chromatograph (F&M Scientific Co.) equipped with a

Brown Elektronik recorder (Minneapolis-Honeywell).

Operating Conditions

Detector cell temperature, °C.	300
Detector cell current, ma.	160
Injection port temperature, °C.	330
Helium flow at exit, cc./minute	85
Column temperature, °C.	190

An 8-ft. length of $\frac{1}{4}$ -inch copper tubing was packed with 10% diethylene glycol succinate on acid washed chromosorb W. The column was conditioned at 200°C. until bleeding was at a minimum.

Isolation of Fatty Acids and Esterification

The sample is treated using ASTM Method D 555-54 for determination of unsaponifiable matter in drying oils. After the unsaponifiable has been separated, the water layers are combined and made acid with 18 N H₂SO₄. The liberated fatty acids are extracted using 75, 50, and 50 ml. portions of chloroform and the combined chloroform extracts washed with 50 ml. aliquots of water until acid free. Evaporate chloroform in 60° water bath with a slow current of inert gas flowing over surface of sample. Bring to constant weight in 60° vacuum oven.

The method of Metcalf and Schmitz (6) using boron trifluoride-methanol reagent is used to prepare the esters because it is rapid, simple and less hazardous than other procedures. This method is simplified still further by substituting boron trifluoride ethyl ether (purified) for boron trifluoride gas.

III. RESULTS

The detector response is not the same for different methyl esters and calibration is necessary when a thermal conductivity detector is used. Methyl palmitate is assigned the correction factor of 1.0 and all the other methyl esters are related to it. The correction factors obtained experimentally by running known weights of pure methyl esters were in good agreement with the calculated values obtained using the equations described by Horrocks, Cornwell and Brown (4).

Refined coconut oil fatty acids were adulterated with commercial dimer acids and examined before and after adulteration by gas chromatography using an internal standard. This was done to establish the feasibility of using an internal standard when examining methyl esters containing materials of extremely low vapour pressures. Dimer acids are C₃₆ acids and are the type that would be encountered in fatty acids extracted from heat bodied oils and alkyd resins. The results are shown in Table I and the necessity for using an internal standard is illustrated by the comparison with total area results.

Table II shows a comparison of the methods for the determination of fatty acids from a soybean alkyd. Two different alkyds prepared from linseed oil were analyzed and the total area and internal standardization figures given in Table III. Duplicate results were obtained by repeating the entire procedure and not

just the gas chromatography step. The total area results are in error and the amount of polymerized fatty acids formed is not apparent.

Heat bodied and cyclopentadiene treated oils were tested and the lower fatty acids values obtained with an internal standard are shown in Tables IV and V and indicates that a high percentage of polymerized material is present. A modified total area method (7), which provides approximate results, was used to confirm that the internal standard results were in proper alignment. The 95% confidence interval statistical method (1) was applied to the results from the modified total area technique and gave a 40% to 46% range for heat bodied fatty acids and 35% to 43% range for the cyclopentadiene treated fatty acids. The broad range is indicative of poor reproducibility from three observations.

IV. DISCUSSION

Varying amounts of polymerized fatty acids will form when drying oils are incorporated into coating resins. The total area gas chromatographic procedure is inadequate when polymerized fatty acids are present and it is necessary to analyze these materials by gas chromatography using an internal standard. Margaric acid, a C₁₇ carboxylic acid, is not natural occurring and forms a methyl ester possessing a retention time different than the natural occurring acids, thus making it suitable as an internal standard.

V. REFERENCES

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APPENDIX

Tables

TABLE I

GAS CHROMATOGRAPHIC ANALYSIS OF A MIXTURE OF COCONUT OIL FATTY ACIDS
AND DIMER ACIDS USING THE INTERNAL STANDARD METHOD

Methyl Ester	Found %
Caprylate	6.8
Caprate	4.9
Laurate	45.4
Myristate	15.7
Palmitate	7.6
Stearate	4.1
Oleate	4.8
Linoleate	<u>0.9</u>
Total	90.2*

*Mixture contained 90.1% coconut fatty acids and 9.8% dimer acids.

TABLE II

ANALYSIS OF SOYBEAN OIL FATTY ACIDS FROM ALKYD RESIN COMPARISON
OF INTERNAL STANDARD AND TOTAL AREA METHODS

Methyl Ester	Internal Standard %	Total Area %
Palmitate	15.0	16.8
Stearate	3.7	4.2
Oleate	19.3	21.7
Linoleate	45.7	51.3
Linolenate	4.4	4.9
Miscellaneous	<u>0.9</u>	<u>1.1</u>
Total	89.0	100.0

TABLE III

ANALYSIS OF LINSEED OIL FATTY ACIDS FROM ALKYD RESINS
COMPARISON OF INTERNAL STANDARD AND TOTAL AREA METHODS

Methyl Ester	Alkyd A				Alkyd B			
	Method 1*		Method 2**		Method 1		Method 2	
	%		%		%		%	
Palmitate	5.7;	5.6	7.4;	7.3	6.1;	5.9	6.8;	6.6
Stearate	3.6;	3.5	4.7;	4.4	4.1;	3.8	4.6;	4.2
Oleate	19.5;	19.3	25.5;	25.2	21.0;	20.5	23.0;	23.0
Linoleate	13.0;	13.2	17.3;	17.1	15.4;	15.8	17.3;	17.5
Linolenate	33.2;	34.4	44.3;	45.0	42.5;	43.5	47.7;	48.7
Miscellaneous	0.7;	0.7	0.8;	0.9				
Total	75.7	76.7	100.0	100.0	89.1	89.5	100.0	100.0

* Internal standard.

** Total area.

TABLE IV

ANALYSIS OF HEAT BODIED LINSEED OIL
COMPARISON OF INTERNAL STANDARD AND TOTAL AREA METHODS

Methyl Ester	Internal Standard		Total Area		Modified Total Area*	
	%		%		%	
Palmitate	5.5		11.5		---	
Stearate	4.2		8.5		---	
Oleate	18.5		39.5		---	
Linoleate	9.7		20.1		---	
Linolenate	<u>9.8</u>		<u>20.4</u>		<u>---</u>	
Total	47.7		100.0		43.0	

* Method (7) produces approximate results.

TABLE V

ANALYSIS OF CYCLOPENTADIENE TREATED OIL
COMPARISON OF INTERNAL STANDARD AND TOTAL AREA METHODS

Methyl Ester	Internal Standard %	Total Area %	Modified Total Area*
Palmitate	5.3	14.7	--
Stearate	3.7	10.2	--
Oleate	15.2	41.0	--
Linoleate	6.5	18.5	--
Linolenate	<u>5.6</u>	<u>15.6</u>	<u>--</u>
Total	36.3	100.0	39.0

* Method (7) produces approximate results.

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